

Lack of Stability in the Stillinger-Weber Analysis, and a Stable Analysis of the Potential Energy Landscape

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Abstract

We examine the Stillinger-Weber analysis of the potential energy landscape for its stability and conclude that it does not provide a stable description of the system as the free energy slope and curvature vanish simultaneously. An alternative analysis developed recently by us involving complexity provides a stable description with complexity a monotonic increasing function of temperature.

It is well known that most supercooled liquids (SCL) become viscous when their configurational entropy becomes negligible as they are cooled, provided the corresponding crystal is not allowed to nucleate. Our current understanding of glassy behavior is still far from complete, even after many decades of continuous investigation. In order to better understand the flow properties of viscous fluids, Goldstein proposed the potential energy landscape (PEL) picture using *classical canonical ensemble* [1, 2] to qualitatively discuss an interesting but sufficiently tractable scheme to study SCL and the glassy states by drawing attention to the potential energy minima (having the energy \mathcal{E}), to be called basin minima (BM) in the following. The landscape picture with its BM's plays a pivotal role not only in the thermodynamics of viscous fluids at *low temperatures* but in many disparate fields like glasses, proteins and clusters [3], and has established itself as an important thermodynamic approach in theoretical physics. Thus, it is highly desirable to understand the significance of this approach. Stillinger and Weber (SW) extended the work of Goldstein to higher temperatures by carrying out a formal analysis in terms of the minima energies \mathcal{E} [4, 5]. Their analysis has given rise to a considerable amount of literature in recent years; for a partial list, see [4, 5, 6, 7]. Many of the numerous numerical evidence [7] appear to be consistent with Goldstein's seminal ideas [1].

In this work, we study the stability of the SW analysis, which seems not to have been investigated in the literature. There are two different conditions for the stability of a thermodynamic theory [8]. The first one is the vanishing of the slope of the free energy function and is commonly discussed in the literature. The other condition is of a strictly positive curvature of the free energy function at the point where the first condition is met. This does not appear to have been ever discussed. To our surprise, we find that the free energy function in the SW analysis has a zero curvature. Thus, the SW analysis does not give rise to a stable description of the system and must be replaced by other self-consistent approaches. We have recently developed such an approach [9, 10], which borrows the concept of complexity developed for spin glasses [11, 12]. The new analysis has no problem with stability and is consistent.

Conventional Approach. The canonical PF $Z(T)$ for a

system of N particles in a volume V is

$$Z(T) \equiv \sum_E W(E) e^{-\beta E}, \quad (1)$$

where $W(E)$ represents the number of configurations of energy E and defines the microcanonical entropy $S(E) \equiv \ln W(E)$, and β is the inverse temperature in the units of the Boltzmann constant. The value of $Z(T)$ for a macroscopic system, which is what we consider here, is determined by the dominant term in the sum, which is located at the equilibrium energy $\bar{E} \equiv E(T)$: $Z(T) \cong W(\bar{E}) \exp(-\beta \bar{E})$. The determination of \bar{E} for a macroscopic system is simplified by noting that E is almost a continuous variable for a macroscopic system. In terms of $S(E)$, \bar{E} is given by the *location of the minimum* of the free energy function $F(T, E) = E - TS(E)$ at fixed T . In equilibrium, the entropy $S(T) \equiv S(E = \bar{E})$ and free energy $F(T) \equiv F(T, \bar{E}) = E(T) - TS(T)$ become functions only of T . The conditions for the minimum are $[\partial F(T, E)/\partial E]_T = 0$, and $[\partial^2 F(T, E)/\partial E^2]_T > 0$ leading to

$$[\partial S(E)/\partial E]_{E=E(T)} = \beta, \quad \partial S(T)/\partial T > 0, \quad (2)$$

which are always satisfied because of a non-negative heat capacity. With the use of (2), we immediately conclude

$$T(\partial S(T)/\partial T) = \partial E(T)/\partial T, \quad (3)$$

which is consistent with the first law of thermodynamics at constant V , and N .

At a given temperature T , only those configurations that have the energy $E = \bar{E}$ (or within a narrow width around it, depending on the heat capacity; we will neglect this width here) determine the thermodynamics through the entropy $S(T)$. All energies other than \bar{E} and, therefore, all configurations not included in $W(\bar{E})$ are irrelevant at T . Thus, thermodynamics is highly *selective*. This will remain true even in the landscape picture, where the equilibrium states will have the same energy regardless of which basin they belong to. Thus, $\bar{E} = E(T)$ *cannot depend explicitly on the basin minima energy \mathcal{E}* : $(\partial \bar{E} / \partial \mathcal{E})_T = 0$.

Goldstein's Approximate Analysis. In his analysis, Goldstein has listed two conjectures that were common in

the field [2] at the time: the basin PF $z_b(T)$ is (i) independent of the basin's minimum energy \mathcal{E} , and (ii) insensitive to the basins being explored. Utilizing these assumptions, Goldstein has expressed the PF as a product [2] of the basin and BM PF'

$$Z(T) = z_b(T)Z_{\text{BM}}(T); \quad (4)$$

here z_b for a given basin is defined by considering shifted energies $E - \mathcal{E}$ with respect to the minimum energy \mathcal{E} of that basin; see also Schulz [13]. Goldstein has emphasized that basin anharmonicity or the curvature at its minimum [14] may be very important. These are included in z_b , so that it is determined by the entire basin topology. According to Goldstein, all equilibrium basins have the same equilibrium basin free energy $f_b(T) \equiv -T \ln z_b$. The BM-PF is defined [2, 13] as

$$Z_{\text{BM}}(T) = \sum_{\mathcal{E}} N_{\text{BM}}(\mathcal{E}) e^{-\beta \mathcal{E}}. \quad (5)$$

Here, $N_{\text{BM}}(\mathcal{E})$ represents the number of basins whose BM are at energy \mathcal{E} . The equilibrium BM energy $\bar{\mathcal{E}} = \mathcal{E}(T)$ is the value of \mathcal{E} at which the summand in (5) is maximum. The conditions for the maximum in terms of the BM entropy $S_{\text{BM}}(\mathcal{E}) \equiv \ln N_{\text{BM}}(\mathcal{E})$ are given by

$$[\partial S_{\text{BM}}(\mathcal{E})/\partial \mathcal{E}]_{\mathcal{E}=\bar{\mathcal{E}}} = \beta, \quad \partial \bar{\mathcal{E}}/\partial T > 0, \quad (6)$$

which are the standard conditions of equilibrium; compare with (2). Thus, the analysis is completely stable in this approximation. It is clear that the BM description proposed by Goldstein ensures that $\bar{\mathcal{E}}$ is a monotonic increasing function of T . Since this approximation is expected to be good at low temperatures, we expect $\bar{\mathcal{E}}$ to be monotonic increasing there. But it need not be true at all temperatures as shown below, thereby limiting the usefulness of the BM-description at all temperatures that has been formally adopted by Stillinger and Weber to which we now turn.

SW Analysis. A basin is indexed by j , and the lowest and highest basin energies are denoted by \mathcal{E}_j , and \mathcal{E}'_j , respectively, so that the basin does not exist outside the energy range $\Delta_j E \equiv (\mathcal{E}_j, \mathcal{E}'_j)$. Let $W_j(E)$ ($E \in \Delta_j E$) represent the number of distinct configurations of energy E in the j -th basin and introduce the entropy $S_j(E) \equiv \ln W_j(E)$. We now introduce the *shifted* PF

$$z_j(T) \equiv \sum_{E \in \Delta_j E} W_j(E) e^{-\beta(E-\mathcal{E}_j)} \quad (7)$$

of the j -th basin and the free energy function $f_j(\mathcal{E}_j, E, T) \equiv E - \mathcal{E}_j - TS_j(E)$, determined by the general summand in (7). The form of $f_j(\mathcal{E}_j, E, T)$ assumes that \mathcal{E}_j, E are *independent*, which is consistent with what was said above about the energy $\bar{\mathcal{E}}$ of equilibrium configurations and its independence from the basins

to which they belong. The conditions for the minimum of $f_j(\mathcal{E}_j, E, T)$ at $E = \bar{E}_j \equiv E_j(T)$ are

$$(\partial f_j(\mathcal{E}_j, E, T)/\partial E)_{\mathcal{E}_j, T} \Big|_{E=\bar{E}_j} = 0, \quad (8a)$$

$$(\partial^2 f_j(\mathcal{E}_j, E, T)/\partial E^2)_{\mathcal{E}_j, T} \Big|_{E=\bar{E}_j} > 0, \quad (8b)$$

and simplify to

$$(\partial S_j(E)/\partial E)_{\mathcal{E}_j} \Big|_{E=\bar{E}_j} = \beta, \quad \partial E_j(T)/\partial T > 0. \quad (9)$$

Both conditions are always met. The *average* basin energy $E_j(T)$ determines the average entropy $S_j(T) \equiv S_j(E = \bar{E}_j)$, so that $f_j(T) \equiv -T \ln z_j(T) = E_j(T) - \mathcal{E}_j - TS_j(T)$ represents the basin free energy. We wish to emphasize that $E_j(T), S_j(T)$, and $f_j(T)$ do *not* represent equilibrium quantities yet; the latter are determined only after $Z(T)$ is evaluated. (If each basin is treated as representing an independent system in a formal sense, then these quantities do represent equilibrium values for the particular basin.)

We now group basins, indexed by $j(\lambda)$, into basin classes (BC) \mathcal{B}_λ , indexed by λ , so that all basins in a class have the same BM energy $\mathcal{E} = \mathcal{E}_\lambda$. The basins in a class do *not* have to be close in the configuration space. The number of basins in \mathcal{B}_λ is $N_{\text{BM}}(\mathcal{E}_\lambda)$, and the corresponding BM entropy is $S_{\text{BM}}(\mathcal{E}_\lambda) \equiv \ln N_{\text{BM}}(\mathcal{E}_\lambda)$. Let

$$Z_\lambda(T) \equiv \sum_{j \in j(\lambda)} z_j(T), \quad z_\lambda \equiv Z_\lambda(T)/N_{\text{BM}}(\mathcal{E}_\lambda), \quad (10)$$

denote the shifted and the mean shifted basin \mathcal{B}_λ -PF, respectively, so that

$$Z(T) \equiv \sum_{\lambda} e^{-\beta \mathcal{E}_\lambda + S_{\text{BM}}(\mathcal{E}_\lambda)} z_\lambda(T), \quad (11a)$$

$$\mathcal{E}(T) \equiv \sum_{\lambda} \mathcal{E}_\lambda e^{-\beta \mathcal{E}_\lambda + S_{\text{BM}}(\mathcal{E}_\lambda)} z_\lambda(T)/Z(T). \quad (11b)$$

Here, $\bar{\mathcal{E}} = \mathcal{E}(T)$ represents the equilibrium BM energy. It is easy to see that $\partial \bar{\mathcal{E}}/\partial T$ is a cross-correlation so that it need not have a unique sign [10]. The equilibrium free energy, entropy and energy are $F(T) = -T \ln Z(T)$, $S(T) = -\partial F/\partial T$ and $E(T) = F(T) + TS(T)$, respectively.

SW Assumption. In the SW analysis, the sum over λ in (11a,11b) is replaced by a sum over the BM energy \mathcal{E}_λ by assuming that z_λ depends explicitly on \mathcal{E}_λ in addition to T : $z_\lambda = z_\lambda(\mathcal{E}_\lambda, T)$. This issue has been examined earlier by us [9, 10]. Here, we pursue the consequence of this *assumption* for the stability of this approach. Let $f_\lambda(\mathcal{E}_\lambda, T) = -T \ln z_\lambda(\mathcal{E}_\lambda, T)$ be the mean free energy resulting from the mean basin PF z_λ and $S_\lambda(\mathcal{E}_\lambda, T) = -[\partial f_\lambda(\mathcal{E}_\lambda, T)/\partial T]_{\mathcal{E}_\lambda}$ the mean basin entropy. From the form of $Z_\lambda(T)$ and $z_\lambda(\mathcal{E}_\lambda, T)$, it is obvious that we can rewrite $z_\lambda(\mathcal{E}_\lambda, T)$ as follows:

$$z_\lambda(\mathcal{E}_\lambda, T) = \sum_{E \in \Delta_\lambda E} W_\lambda(E) e^{-\beta(E-\mathcal{E}_\lambda)-S_{\text{BM}}(\mathcal{E}_\lambda)}, \quad (12)$$

where $W_\lambda(E)$ represents the number of configurations of energy E that belong to \mathcal{B}_λ and indicated by $E \in \Delta_\lambda E$. Introducing $S_\lambda(\mathcal{E}_\lambda, E) \equiv \ln W_\lambda(E) - S_{\text{BM}}(\mathcal{E}_\lambda)$, we find that the general summand in (12) determines a mean free energy function $f_\lambda(\mathcal{E}_\lambda, E, T) \equiv E - \mathcal{E}_\lambda - TS_\lambda(\mathcal{E}_\lambda, E)$ whose minimization with respect to E at fixed \mathcal{E}_λ , and T determines the mean free energy $f_\lambda(\mathcal{E}_\lambda, T)$. Let $\bar{E}_\lambda = E_\lambda(T)$ denote the location of the minimum, the conditions for which are exactly the same as for $f_j(\mathcal{E}_j, E, T)$ above, except that the index j is replaced by λ and $S_\lambda(\mathcal{E}_\lambda, E)$ is a two-variable function. Again, \mathcal{E}_λ , and E are treated as two independent variables for the minimization to be carried out. The conditions for minimization are

$$(\partial S_\lambda(\mathcal{E}_\lambda, E)/\partial E)|_{E=\bar{E}_\lambda} = \beta, \quad \partial E_\lambda(T)/\partial T > 0. \quad (13)$$

The mean free energy and entropy are given by $f(\mathcal{E}_\lambda, T) \equiv f_\lambda(\mathcal{E}_\lambda, \bar{E}_\lambda, T) \equiv \bar{E}_\lambda - \mathcal{E}_\lambda - TS_\lambda(\mathcal{E}_\lambda, \bar{E}_\lambda)$ and $S_\lambda(\mathcal{E}_\lambda, T) = S_\lambda(\mathcal{E}_\lambda, \bar{E}_\lambda)$, respectively. It is easy to see that

$$S_\lambda(\mathcal{E}_\lambda, \bar{E}_\lambda) = -[\partial f_\lambda(\mathcal{E}_\lambda, T)/\partial T]_{\mathcal{E}_\lambda} \quad (14)$$

as expected, where we must use

$$(\partial \bar{E}_\lambda/\partial T) = T[\partial S_\lambda(\mathcal{E}_\lambda, \bar{E}_\lambda)/\partial T]_{\mathcal{E}_\lambda}, \quad (15)$$

which follows immediately from the first condition in (13). Since \bar{E}_λ is independent of \mathcal{E}_λ at fixed T , we can differentiate $f_\lambda(\mathcal{E}_\lambda, \bar{E}_\lambda, T)$ with respect to \mathcal{E}_λ to obtain

$$(\partial S(\mathcal{E}, T)/\partial \mathcal{E})_T = -\beta[1 + (\partial f(\mathcal{E}, T)/\partial \mathcal{E})_T], \quad (16)$$

where fixed T means keeping \bar{E}_λ and T fixed simultaneously, and where we have suppressed λ to treat \mathcal{E} a variable.

Zero-Slope Condition. Because of the assumed \mathcal{E} -dependence of $z_\lambda(T)$, the general summand in (11a, 11b) becomes an explicit function of \mathcal{E} , and we can minimize the corresponding free energy function $F_B(\mathcal{E}, T) \equiv \mathcal{E} + f(\mathcal{E}, T) - TS_{\text{BM}}(\mathcal{E})$ with respect to \mathcal{E} at fixed T to determine $Z(T)$. The minimum of $F_B(\mathcal{E}, T)$ is given by the conditions $[\partial F_B(\mathcal{E}, T)/\partial \mathcal{E}]_T = 0$, and $[\partial^2 F_B(\mathcal{E}, T)/\partial \mathcal{E}^2]_T > 0$. The first condition is satisfied at the equilibrium BM-energy $\bar{\mathcal{E}} = \mathcal{E}(T) = \mathcal{E}(T)$, see (11b). It is also given by the solution of

$$\partial S_{\text{BM}}(\mathcal{E})/\partial \mathcal{E} = \beta[1 + (\partial f(\mathcal{E}, T)/\partial \mathcal{E})_T], \quad (17)$$

and determines the equilibrium free energy $F(T) \equiv F_B(\bar{\mathcal{E}}, T)$, BM-entropy $S_{\text{BM}}(T) \equiv S_{\text{BM}}(\mathcal{E} = \bar{\mathcal{E}})$, mean basin free energy $f_b(T) = f(\bar{\mathcal{E}}, T)$ and mean basin entropy $S_b(T) = S(\bar{\mathcal{E}}, T) = -[\partial f(\bar{\mathcal{E}}, T)/\partial T]_{\mathcal{E}}$; see (14). The equilibrium mean basin energy $E_b(T)$ is obtained by the fundamental relation $E_b(T) - \bar{\mathcal{E}} = f_b(T) + TS_b(T)$. It is easy to see that the form of the equilibrium free energy $F(T) = f(\bar{\mathcal{E}}, T) + \mathcal{E}(T) - TS_{\text{BM}}(\bar{\mathcal{E}})$ is the same as the free energy obtained by Goldstein in (4), except that the equations determining the equilibrium BM-energy are different; compare (6) and (17). The two conditions become

identical if f is taken to be independent of \mathcal{E} , as was assumed by Goldstein. Comparing (17) with (16) applied at $\mathcal{E} = \bar{\mathcal{E}}$, we obtain an interesting relation

$$\partial S_{\text{BM}}(\bar{\mathcal{E}})/\partial \bar{\mathcal{E}} + (\partial S(\bar{\mathcal{E}}, T)/\partial \bar{\mathcal{E}})_T = 0, \quad (18)$$

which will play a very important role in the following when we investigate the stability of this approach.

The entropy $S(T)$ can now be obtained by using the relation $S(T) = -\partial F(T)/\partial T$. We immediately find that $S(T) = S(\bar{\mathcal{E}}, T) + S_{\text{BM}}(\bar{\mathcal{E}})$. The equilibrium energy given by $F(T) + TS(T)$, thus, turns out to be $E_b(T)$ introduced above. From the conventional analysis, this energy was identified as $E(T)$. Thus,

$$E_b(T) \equiv E(T).$$

Now, we apply (15) at $\bar{E}_\lambda = E_b(T) \equiv E(T)$ to find

$$(\partial E(T)/\partial T) = T[\partial S(\bar{\mathcal{E}}, \bar{E})/\partial T]_{\bar{\mathcal{E}}}. \quad (19)$$

It should be noted that the entropy derivative on the right-hand side is the intrabasin change in the basin entropy with T without leaving the basin (fixed $\bar{\mathcal{E}}$). Comparing this with (3), we find that the right hand side in both equations must be the same. This can only happen if (18) is fulfilled; we assume that $(\partial \bar{\mathcal{E}}/\partial T) \neq 0$. This provides another justification for the validity of (18), and is merely a consequence of the first condition of stability.

Curvature Condition. We now proceed to discuss the second condition for minimization. This condition of stability at $\mathcal{E} = \bar{\mathcal{E}}$ reads

$$(\partial^2 f(\bar{\mathcal{E}}, T)/\partial \bar{\mathcal{E}}^2)_T - T(\partial^2 S_{\text{BM}}(\bar{\mathcal{E}})/\partial \bar{\mathcal{E}}^2) > 0. \quad (20)$$

We differentiate (17) at arbitrary \mathcal{E} , which yields

$$\begin{aligned} \frac{\partial^2 S_{\text{BM}}(\mathcal{E})}{\partial \mathcal{E}^2} &= \frac{\partial \beta}{\partial \mathcal{E}}[1 + (\frac{\partial f(\mathcal{E}, T)}{\partial \mathcal{E}})_T] + \\ &\quad \beta[(\frac{\partial^2 f(\mathcal{E}, T)}{\partial \mathcal{E}^2})_T + \frac{\partial^2 f(\mathcal{E}, T)}{\partial T \partial \mathcal{E}} \frac{\partial T}{\partial \mathcal{E}}]. \end{aligned}$$

We now set $\mathcal{E} = \bar{\mathcal{E}}$ and use it in (20) to finally obtain the condition to be

$$[\partial S_{\text{BM}}(\bar{\mathcal{E}})/\partial \bar{\mathcal{E}} - \partial^2 f(\bar{\mathcal{E}}, T)/\partial \bar{\mathcal{E}} \partial T](\partial T/\partial \bar{\mathcal{E}}) > 0, \quad (21)$$

where we have used (17). Applying (14) at equilibrium, we obtain $S(\bar{\mathcal{E}}, T) = -[\partial f(\bar{\mathcal{E}}, T)/\partial T]_{\bar{\mathcal{E}}}$. Thus, the numerator in (21) can be reduced to $\partial S_{\text{BM}}(\bar{\mathcal{E}})/\partial \bar{\mathcal{E}} + [\partial S(\bar{\mathcal{E}}, T)/\partial \bar{\mathcal{E}}]_T$. [The numerator can also be alternatively expressed as $\partial S(T)/\partial \bar{\mathcal{E}} - [\partial S(\bar{\mathcal{E}}, T)/\partial T]_{\bar{\mathcal{E}}} / (\partial \bar{\mathcal{E}}/\partial T)$ where $S(T) = S(\bar{\mathcal{E}}, T) + S_{\text{BM}}(\bar{\mathcal{E}})$]. Thus, the second condition of stability reads

$$[\partial S_{\text{BM}}(\bar{\mathcal{E}})/\partial \bar{\mathcal{E}} + [\partial S(\bar{\mathcal{E}}, T)/\partial \bar{\mathcal{E}}]_T](\partial T/\partial \bar{\mathcal{E}}) > 0, \quad (22)$$

which can never be satisfied in view of (18) unless $(\partial \bar{\mathcal{E}}/\partial T) = 0$. Since it is evident from (11b) that $(\partial \bar{\mathcal{E}}/\partial T) \neq 0$ in general, we conclude that the curvature

of the free energy function at $\mathcal{E} = \bar{\mathcal{E}}$ must vanish on account of the first condition of stability. Thus, we have finally shown that the SW analysis is internally inconsistent and fails to provide a stable description of the system.

Complexity Approach. We provide an alternative approach [10] which, as we show below, turns out to be a consistent and stable approach. We consider the *unshifted* basin partition function $Z_j(T) \equiv e^{\beta \mathcal{E}_\lambda} z_j(T)$ and introduce the unshifted basin free energy $\varphi_j(T) = -T \ln Z_j(T)$. The conditions of stability for the basin free energy $\varphi_j(E, T) \equiv E - TS_j(E)$ are given in (9). The basin free energy $\varphi_j(T)$ varies from basin to basin and represents a family of functions, one for each j . Let $\mathcal{N}(\varphi, T)$ represent the number of basins having the same free energy φ for a given T and rewrite (1) as

$$Z(T) \equiv \sum_{\varphi} \mathcal{N}(\varphi, T) e^{-\beta \varphi}. \quad (23)$$

The *complexity* is defined by $\mathcal{S}(\varphi, T) \equiv \ln \mathcal{N}(\varphi, T)$, in terms of which the conditions of stability at $\varphi = \bar{\varphi}_b = \varphi_b(T)$

$$(\partial \mathcal{S}(\varphi, T) / \partial \varphi)_T \Big|_{\varphi=\bar{\varphi}_b} = \beta, [\partial^2 \mathcal{S}(\bar{\varphi}_b, T) / \partial \bar{\varphi}_b^2]_T < 0. \quad (24)$$

The equilibrium complexity $\bar{\mathcal{S}}(T)$ is given by $\mathcal{S}(\bar{\varphi}_b, T)$ evaluated at $\varphi = \bar{\varphi}_b$. We consider the case so that $\mathcal{S}(\varphi, T)$ can be inverted at fixed T to express φ as a function of $\mathcal{S}, T : \varphi = \varphi(\mathcal{S}, T)$. Thus,

$$d\varphi(\mathcal{S}, T) = (\partial \varphi / \partial \mathcal{S})_T d\mathcal{S} + (\partial \varphi / \partial T)_S dT. \quad (25)$$

At equilibrium, $\bar{\varphi}_b = \varphi(\bar{\mathcal{S}}, T)$, and the coefficient of the first term becomes T according to the first relation in (24). In general, the coefficient of the second term is the negative basin entropy: $S(\varphi, T) = -(\partial \varphi / \partial T)_S$; compare with (14). Let us introduce $\sigma(\varphi, T) = (\partial \mathcal{S}(\varphi, T) / \partial \varphi)_T$ so that $\sigma(\bar{\varphi}_b, T) = \beta$ at equilibrium. From (25), we find

$$\begin{aligned} (\partial \mathcal{S}(\varphi, T) / \partial T)_\varphi &= -\partial \mathcal{S}(\varphi, T) / \partial \varphi_T (\partial \varphi(\mathcal{S}, T) / \partial T)_S \\ &= \sigma(\varphi, T) S(\varphi, T). \end{aligned} \quad (26)$$

We differentiate $\sigma(\varphi, T)$ with respect to T at constant φ and use the above equation to obtain

$$\begin{aligned} (\partial \sigma(\varphi, T) / \partial T)_\varphi &= \partial^2 \mathcal{S}(\varphi, T) / \partial \varphi \partial T \\ &= (\partial [\sigma(\varphi, T) S(\varphi, T)] / \partial \varphi)_T, \end{aligned}$$

which is used to calculate

$$\begin{aligned} \partial \sigma(\varphi, T) / \partial T &= (\partial \sigma(\varphi, T) / \partial \varphi)_T [(\partial \varphi / \partial T) + S(\varphi, T)] \\ &\quad + \sigma(\varphi, T) (\partial S(\varphi, T) / \partial \varphi)_T. \end{aligned}$$

We now differentiate the first condition in (24) and use the above equation at equilibrium to obtain

$$\begin{aligned} (\partial \sigma(\bar{\varphi}_b, T) / \partial \bar{\varphi}_b)_T [(\partial \bar{\varphi}_b / \partial T) + S(\bar{\varphi}_b, T)] \\ = -\beta^2 - \beta (\partial S(\bar{\varphi}_b, T) / \partial \bar{\varphi}_b)_T. \end{aligned}$$

The basin entropy $S(\varphi, T)$ can also be expressed as $S(\mathcal{S}, T)$, so that the basin free energy function can be written as $\varphi(\mathcal{S}, T) = E(T) - TS(\mathcal{S}, T)$. From this, we obtain

$$(\partial \varphi(\mathcal{S}, T) / \partial \mathcal{S})_T = -T (\partial S(\mathcal{S}, T) / \partial \mathcal{S})_T.$$

At equilibrium ($\mathcal{S} = \bar{\mathcal{S}}$), the left-hand side is equal to T from the first condition in (24). Thus, at equilibrium,

$$(\partial S(\bar{\mathcal{S}}, T) / \partial \bar{\mathcal{S}})_T = -1.$$

Since $(\partial S(\bar{\varphi}_b, T) / \partial \bar{\varphi}_b)_T = (\partial S(\bar{\mathcal{S}}, T) / \partial \bar{\mathcal{S}})_T (\partial \bar{\mathcal{S}} / \partial \bar{\varphi}_b) = -(\partial S(\bar{\varphi}_b, T) / \partial \bar{\varphi}_b) = -[\beta + (\partial S / \partial T)_{\bar{\varphi}_b} (\partial T / \partial \bar{\varphi}_b)] = -\beta[1 + S_b(T) (\partial T / \partial \bar{\varphi}_b)]$, where we have used (26) at equilibrium [$\sigma(\bar{\varphi}_b, T) = \beta$, and $S_b(T) = S(\bar{\varphi}_b, T)$]. Thus, we find that

$$\begin{aligned} &(\partial \sigma(\bar{\varphi}_b, T) / \partial \bar{\varphi}_b)_T [(\partial \bar{\varphi}_b / \partial T) + S_b(T)] \\ &= \beta^2 S_b(T) (\partial T / \partial \bar{\varphi}_b), \end{aligned}$$

so that the second condition of stability becomes

$$\begin{aligned} &(\partial \sigma(\bar{\varphi}_b, T) / \partial \bar{\varphi}_b)_T = \beta^3 S_b(T) (\partial T / \partial \bar{\varphi}_b) / (\partial \bar{\mathcal{S}} / \partial T) \\ &< 0, \end{aligned}$$

where we have used the relation

$$T (\partial \bar{\mathcal{S}} / \partial T) = \partial \bar{\varphi}_b / \partial T + S_b(T) \quad (27)$$

obtained from (25). Therefore, the second condition of stability finally becomes

$$(\partial \bar{\mathcal{S}} / \partial T) (\partial \bar{\varphi}_b / \partial T) < 0.$$

We expect $(\partial \bar{\mathcal{S}} / \partial T)$ to be positive at low temperatures, so the stability condition there reduces to $(\partial \bar{\varphi}_b / \partial T) < 0$. Because of (27), it is easy to see that $(\partial \bar{\mathcal{S}} / \partial T) > 0$ even if $(\partial \bar{\varphi}_b / \partial T)$ changes sign, so the stability always requires

$$(\partial \bar{\mathcal{S}} / \partial T) > 0; (\partial \bar{\varphi}_b / \partial T) < 0.$$

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